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1-Ferrocenylcyclopropene and 1-ferrocenylcyclopropyl cation

Tatiana Klimova [a], Elena I. Klimova [a,*], Marcos Martínez García [b], Cecilio Alvarez Toledano [b], Ruben Alfredo Toscano [b]

[a] Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Coyoacán, C.P. 04510, Mexico D.F., Mexico
[b] Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Coyoacán, C.P. 04510, Mexico D.F., Mexico

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Abstract

Dehydrobromination of *cis* and *trans* isomers of 1-bromo-2-ferrocenylcyclopropanes affords 1-ferrocenylcyclopropene. Its protonation with HBF_4 results in 1-ferrocenylcyclopropylium tetrafluoroborate, which alkylates *N*,*N*-dimethylaniline in *para* position to yield 1-(*p*-dimethylaminophenyl)-1-ferrocenylcyclopropane. 1-Ferrocenylcyclopropene reacts with 1,3-diphenylisobenzofuran to give the classical [4+2]-cycloaddition product. Its structure as exo-2-ferrocenyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene was established based on the data from X-ray diffraction analysis.

Keywords: Cyclopropene; Cyclopropane; [4+2]-Cycloadduct; Protonation; Alkylation; Cyclopropyl cation; Ferrocene

1. Introduction

All the available literature data suggest that the properties of three-membered carbocycles change upon introduction of a ferrocenyl substituent. Thus properties of ferrocenylcyclopropanes and ferrocenylcyclopropenes are distinctly different from those of unsubstituted carbocycles and analogous arylcyclopropanes and arylcyclopropenes [1–7]. In particular, 3-*p*-tolyl-1,2,3-triferrocenylcyclopropene undergoes small-ring opening followed by cyclization involving ferrocenyl and aryl fragments when heated in chloroform solution at 50 °C [3], while 3-phenyl- and 3-naphthyl-3-ferrocenylcyclopropenes rearrange analogously at ~80 °C to give the corresponding indene derivatives [4,5]. Isomerization of *Z*-1,2-diferrocenyl- and *Z*-1-aryl-2-ferrocenylcyclopropanes into the corresponding stable *E* isomers occurred extremely fast, these were formed quantitatively during registration of the ^{1}H-NMR spectra [6,7].

The enhancement of the stability of electron-deficient centers vicinal to the ferrocenyl group is also noteworthy. The first long-lived α-ferrocenylcyclopropyl cation that was observed by Olah and co-workers [8] at −80 °C underwent virtually no small-ring opening when kept at −40 °C.

The effect of ferrocenyl substituents in small rings is rather well pronounced and their influence is often highly selective, therefore, it was of interest to reveal features of the electronic interaction of the ferrocenyl group with the small ring, which is attractive from both the theoretical point of view and in connection with a search for selective reactions of cyclopropanes and cyclopropenes.

Chemical behavior of 3-alkyl- and 3-aryl-3-ferrocenylcyclopropenes has been investigated in recent years in fairly full detail [4,5,9–12]. At the same time, chemistry of monosubstituted ferrocenylcyclopropenes with the ferrocenyl substituent in positions 1 or 3 of the small ring remains unexplored.

2. Results and discussion

In continuation of our investigations into the chemistry of ferrocenylcyclopropenes, we undertook attempts at the preparation of 1- and 3-ferrocenylcyclopropenes (**1a** and **1b**). Presumably, a mixture of these compounds had to be obtained upon dehydrobromination of 1-bromo-2-ferrocenylcyclopropane (**2**) (Scheme 1).

* Corresponding author. Tel./fax: +52-56225366
E-mail address: klimova@servidor.unam.mx (E.I. Klimova).

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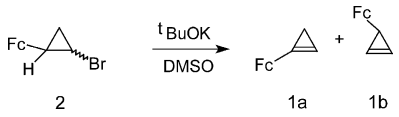


Scheme 1.

The starting monobromides **2** were prepared as follows (Scheme 2).

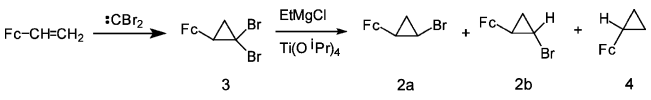
Dibromocyclopropanation of vinylferrocene proceeded without any difficulties, and 1,1-dibromo-2-ferrocenylcyclopropane (**3**) was isolated in high yield (70–80%). This was reduced with a mixture of ethylmagnesium chloride and titanium isopropoxide [11] to give a mixture of *cis*- and *trans*-1-bromo-2-ferrocenylcyclopropanes (**2a** and **2b**) in a 1:1 ratio in 58% yield together with a side product, viz., ferrocenylcyclopropane (**4**) (~ 20%). These could easily be separated by column chromatography on Al_2O_3. NMR spectra of the products obtained proved unambiguously their structures (see Section 3).

The assignment of the isomeric monobromides to the *cis* and *trans* isomeric series has been carried out based on their ^{1}H-NMR spectroscopic data with account of the previously established NMR criteria for the assignment of *Z* and *E* isomers of bromo(ferrocenyl)cyclopropanes [4,5,9–11]. Thus the ^{1}H-NMR spectrum of the monobromide **2a** contains two multiplets at δ 0.81 and 1.34 belonging to the methylene protons. In the ^{1}H-NMR spectrum of the isomeric compound **2b**, analogous signals were present at δ 1.24 and 1.42. The difference in the chemical shifts for the methylene protons in the isomer **2a** ($\Delta\delta = 0.53$ ppm) is larger than that in the isomer **2b** ($\Delta\delta = 0.18$ ppm), which is evidence for the *cis* configuration of the former. Such a regularity has previously been observed in the ^{1}H-NMR spectra of all *Z*- and *E*-isomeric 1-alkyl- and 1-aryl-2-bromo-1-ferrocenylcyclopropanes studied so far [4,5,9–11].

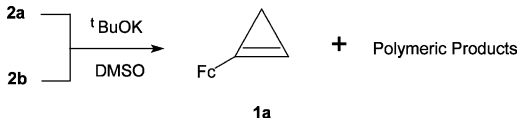
We have found that the reaction of bromo(ferrocenyl)cyclopropanes **2a** and **2b** with potassium *tert*-butoxide in DMSO affords regioselectively 1-ferrocenylcyclopropene **1a** in ~ 41% yield and unidentified polymeric products (Scheme 3).

The cyclopropene **1a** is an orange oily compound unstable on storage. Its structure was established based on the data from ^{1}H-NMR spectroscopy, elemental analysis, and chemical transformations.

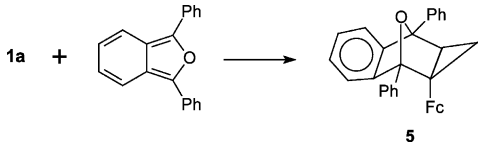
The freshly prepared 1-ferrocenylcyclopropene **1a** reacts with 1,3-diphenylisobensofuran at ambient temperature to give a [4+2]-cycloaddition product **5** (Scheme 4).



Scheme 2.



Scheme 3.



Scheme 4.

Its structure was established based on the spectroscopic data (see Section 3). The ^{1}H- and ^{13}C-NMR spectra correspond to a single structural isomer, which attests to the stereospecific character of the Diels–Alder reaction.

Single crystals of the adduct **5** prepared by crystallization from hexane were studied using X-ray diffraction analysis, which showed that compound **5** has the structure of exo-2-ferrocenyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.02,4]oct-6-ene. The general view of the molecule **5** is shown in Fig. 1. The principal geometrical parameters are listed in Table 1.

We also demonstrated that the protonation of the cyclopropene **1a** with HBF_4 etherate at −40 °C resulted in 1-ferrocenylcyclopropyl tetrafluoroborate **6** (Scheme 5).

The salt **6** is a microcrystalline dark brown substance stable at −40 °C in an inert atmosphere for several hours. We managed to record its ^{1}H-NMR spectrum (for solution in CD_2Cl_2) which corroborated completely the structure **6** (see Section 3).

Like other α-ferrocenylcarbocations [13–16], 1-ferrocenylcyclopropyl cation **6** alkylates *N*,*N*-dimethylaniline in the *para* position to give 1-(*p*-dimethylaminophenyl)-1-ferrocenylcyclopropane (**7**) as the only product (Scheme 6).

The absence of small-ring opening products in this reaction suggests high stabilizing effect of the ferrocenyl substituent with respect to the α-carbocationic center, which imparts sufficient stability even to the cyclopropyl cation **6**. Removal of the ferrocenyl group away from the cationic center to the β-position decreases the stability of the cyclopropyl cations and results in instantaneous three-membered ring opening yielding 1-ferrocenylallyl cations (see Refs. [4–7,9–11]).

3. Experimental

All the solvents were dried according to standard procedures and used freshly distilled. Column chromatography was carried out on alumina (Brockmann

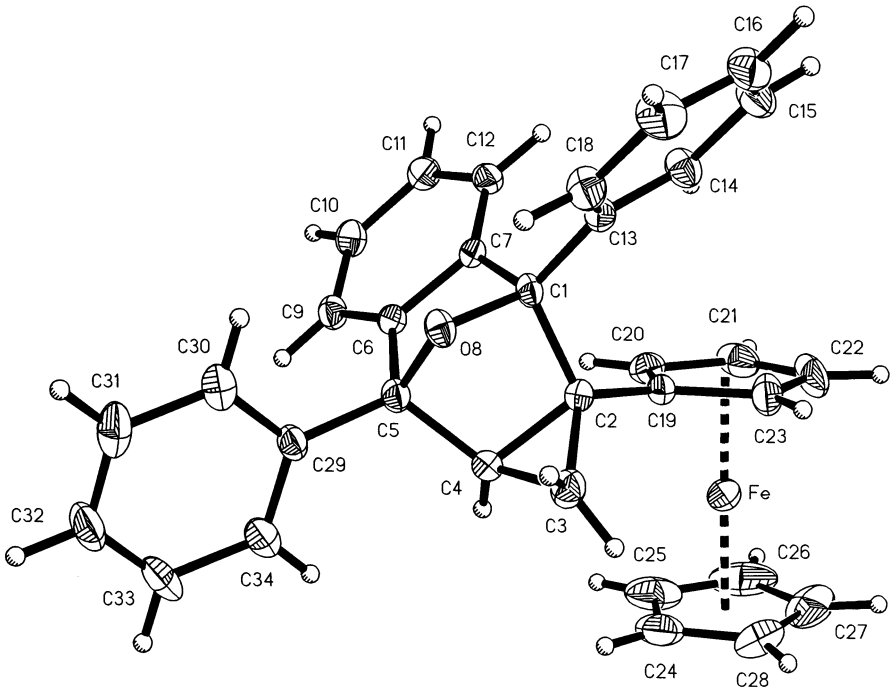
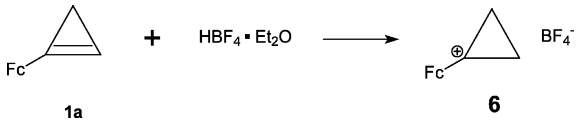


Fig. 1. Crystal structure of **5**.

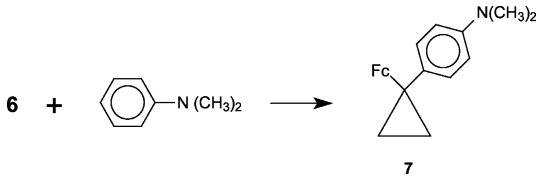
Table 1
Selected bond lengths (Å) and bond angles (°) for compound **5**

Bond lengths, *r*			
C(2)–C(3)	1.519(5)	C(2)–C(4)	1.517(4)
C(3)–C(4)	1.522(5)	C(1)–C(2)	1.579(4)
C(4)–C(5)	1.542(4)	C(5)–C(6)	1.533(5)
C(1)–C(7)	1.532(5)	C(2)–C(19)	1.492(5)
C(5)–C(29)	1.506(4)	C(1)–C(13)	1.512(4)
C(1)–O(8)	1.458(4)	C(5)–O(8)	1.465(4)
Bond angles, ω			
O(8)–C(1)–C(7)	100.1(2)	O(8)–C(1)–C(2)	101.1(2)
C(7)–C(1)–C(2)	104.9(3)	O(8)–C(1)–C(13)	111.9(3)
C(13)–C(1)–C(7)	119.8(3)	C(13)–C(1)–C(2)	116.3(3)
C(19)–C(2)–C(4)	124.7(3)	C(19)–C(2)–C(3)	122.1(3)
C(19)–C(2)–C(1)	118.4(3)	C(3)–C(2)–C(1)	114.6(3)
C(4)–C(2)–C(3)	60.2(2)	C(4)–C(2)–C(1)	102.5(2)
C(2)–C(3)–C(4)	59.9(2)	C(2)–C(4)–C(5)	102.9(3)
C(2)–C(4)–C(3)	59.9(2)	O(8)–C(5)–C(6)	100.1(2)
O(8)–C(5)–C(29)	111.7(3)	O(8)–C(5)–C(4)	101.6(2)
C(6)–C(5)–C(4)	105.2(3)	C(7)–C(6)–C(5)	105.5(3)



Scheme 5.

activity III). The ^{1}H and ^{13}C-NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ with Me_4Si as the internal standard, the ^{1}H-NMR spectrum of the tetrafluoroborate **6** was recorded for a solution in CD_2Cl_2. The following reagents were purchased from Aldrich: bromoform, 99%; ethylmagnesium chloride (2.0 M solution in diethyl ether); potassium *tert*-butoxide, 95%; titanium(IV) isopropoxide (97%); vinylferrocene, 97%; *N*,*N*-dimethylaniline, 99.5%, and dimethyl sulfoxide, anhydrous, 99.8%. Tetrafluoroboric acid etherate, 50–52%, was purchased from Alfa AESAR.



Scheme 6.

The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4/PC diffractometer. The crystallographic data, the parameters of the X-ray diffraction experiment, and refinements are listed in Table 2. The structure of compound **5** was solved by the direct method and refined by the least-squares method in a full-matrix anisotropic approximation for the non-hydrogen atoms.

3.1. 1,1-Dibromo-2-ferrocenylcyclopropane *3*

The title compound was obtained from vinylferrocene according to the standard procedure [9], yield 70–80%, yellow crystals, m.p. 100–102 °C. ^{1}H-NMR, δ: 1.69

Table 2
Crystallographic data and structure refinement parameters for compound **5**

Data	**5**
Molecular formula	$C_{33}H_{26}FeO$
Formula weight	494.39
Temperature (K)	273(2)
Mo-Kα, radiation, λ (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.517(2)
b (Å)	11.268(3)
c (Å)	12.528(3)
α (°)	77.150(10)
β (°)	75.37(2)
γ (°)	74.00(2)
V (Å^3)	1232.6(5)
Z	2
ρ_{calc} (g cm^{-3})	1.332
Absorption coefficient (mm^{-1})	0.636
$F(000)$	516
Monochromator	graphite
θ Scanning range (°)	1.50–25.00
Total number of reflections	4611
Number of independent reflections	4325
R_{int}	0.0388
Goodness of fit on F^2	1.067 (full-matrix least-squares on F^2)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0500$, $wR_2 = 0.1220$
R indices (all data)	$R_1 = 0.0769$, $wR_2 = 0.1420$
Number of refinable parameters	317
Residual electron density (e Å^{-3}), ρ_{min}/ρ_{max}	−0.303/0.404
Weighting scheme	$w = 1/[\sigma^2(F_0^2)+(0.1693P)^2+10.77P]$, where $P = (F_0^2+2F_c^2)/3$

(1H, t, CH_2, $J = 7.8$ Hz), 2.11 (1H, dd, CH_2, $J = 7.8$, 10.8 Hz), 2.68 (1H, dd, CH_2, $J = 7.8$, 10.8 Hz), 4.03 (1H, m, C_5H_4), 4.18 (1H, m, C_5H_4), 4.22 (5H, s, C_5H_5), 4.25 (1H, m, C_5H_4), 4.44 (1H, m, C_5H_4). Anal. Calcd. for $C_{13}H_{12}Br_2Fe$: C, 40.67; H, 3.15; Br, 41.63; Fe, 14.55. Found: C, 40.42; H, 3.28; Br, 41.77; Fe, 14.71%.

3.2. Reduction of the dibromide *3*

A solution of EtMgCl (6 mmol) in ether and several drops of $Ti(OPr^i)_4$ were added with stirring to a solution of the dibromide **3** (1.92 g, 5.0 mmol) in dry tetrahydrofuran (100 ml). The mixture was stirred for 4 h at room temperature (r.t.) and quenched with water (50 ml). The organic layer was separated, washed with water, dried with Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on alumina in hexane and the following products were isolated:

1-Ferrocenylcyclopropane **4**, yield 0.23 g (20.5%), yellow oil. ^{1}H-NMR, δ: 0.47–0.66 (1H, m, CH_2), 0.76–0.80 (1H, m, CH_2), 1.00 (1H, m, CH_2), 1.31 (1H, m, CH_2), 1.53 (1H, m, CH), 4.02 (4H, s, C_5H_4), 4.14 (5H, s, C_5H_5). Anal. Calcd. for $C_{13}H_{14}Fe$: C, 69.05; H, 6.24; Fe, 24.71. Found: C, 68.92; H, 6.39; Fe, 24.90%.

cis-1-Bromo-2-ferrocenylcyclopropane **2a**, yield 0.38 g (25%), yellow crystals, m.p. 60–61 °C. ^{1}H-NMR, δ: 0.81 (1H, m, CH_2), 1.34 (1H, m, CH_2), 1.83 (1H, m, CHFc), 3.03 (1H, m, CH), 3.92 (1H, m, C_5H_4), 3.95 (1H, m, C_5H_4), 3.98 (1H, m, C_5H_4), 4.00 (5H, s, C_5H_5), 4.11 (1H, m, C_5H_4). Anal. Calcd. for $C_{13}H_{13}BrFe$: C, 51.19; H, 4.30; Br, 26.20; Fe, 18.31. Found: C, 51.33; H, 4.12; Br, 26.32; Fe, 18.10%.

trans-1-Bromo-2-ferrocenylcyclopropane **2b**, yield 0.40 g (26%), yellow crystals, m.p. 71–72 °C. ^{1}H-NMR, δ: 1.24 (1H, m, CH_2), 1.42 (1H, m, CH_2), 2.08 (1H, m, CHFc), 2.92 (1H, m, CH), 4.06 (2H, m, C_5H_4), 4.12 (2H, m, C_5H_4), 4.21 (5H, s, C_5H_5). Anal. Calcd. for $C_{13}H_{13}BrFe$: C, 51.19; H, 4.30; Br, 26.20; Fe, 18.31. Found: C, 51.40; H, 4.12; Br, 26.03; Fe, 18.55%.

3.3. Dehydrobromination of bromo(ferrocenyl)cyclopropanes *2a* and *2b*

A mixture of bromo(ferrocenyl)cyclopropane **2a** (or **2b**) (0.9 g, 3 mmol) and Bu^tOK (4 mmol) in DMSO (30 ml) was strirred for 6 h at ~20–25 °C. The reaction mixture was then partitioned between benzene (100 ml) and water (50 ml), the organic layer was washed with water and concentrated in vacuo. Chromatography of the residue (Al_2O_3, hexane) gave 1-ferrocenylcyclopropene **1a**, yield 0.27 g (40%) from the bromide **2a** and 0.28 g (42%) from the bromide **2b**, orange oil. ^{1}H-NMR, δ: 1.00 (1H, m, CH_2), 1.31 (1H, m, CH_2), 1.53 (1H, m, CH), δ 2.61 (2H, d, CH_2, $J = 1.8$ Hz), 4.02 (5H, s, C_5H_5), 4.04 (2H, s, C_5H_4), 4.06 (2H, s, C_5H_4), 6.62 (1H, t, CH=, $J = 1.8$ Hz). Anal. Calcd. for $C_{13}H_{12}Fe$: C, 69.68; H, 5.40; Fe, 24.92. Found: C, 69.86; H, 5.21; Fe, 25.07%.

3.4. Reaction of cyclopropene *1a* with 1,3-diphenylisobenzofuran

A solution of cyclopropene **1a** (0.34 g, 1.5 mmol) and 1,3-diphenylisobenzofuran (0.56 g, 2 mmol) in dry benzene (50 ml) was stirred at r.t. for 48 h. The solvent was evaporated in vacuo and the residue was chromatographed (Al_2O_3, hexane/ether, 7:1) to give the starting cyclopropene (0.12 g, 35%) as an orange oil and the adduct **5**, yield 0.37 g (50%), pale yellow crystals, m.p. 210–211 °C. ^{1}H-NMR, δ: 1.79 (1H, dd, CH, $J = 4.8$, 6.6 Hz), 1.99 (1H, dd, CH_2, $J = 3.6$, 6.6 Hz), 2.29 (1H, dd, CH, $J = 3.6$, 4.8 Hz), 3.05 (1H, m, C_5H_4), 3.93 (1H, m, C_5H_4), 3.99 (5H, s, C_5H_5), 4.03 (1H, m, C_5H_4), 4.08 (1H, m, C_5H_4), 7.10–7.76 (14H, m, 2 C_6H_5, C_6H_4). ^{13}C-

NMR, δ: 21.85 (CH_2); 35.52 (CH_2); 35.59 (C); 66.84, 66.95, 68.94, 70.36 (C_5H_4); 68.28 (C_5H_5); 88.07, 88.15 (C–O); 90.15 ($C_{ipso}Fc$); 119.47, 122.05, 125.45, 126.18, 127.80, 127.83, 127.86, 127.92, 127.93, 127.95, 127.97, 128.35, 128.36, 128.45 (2 C_6H_5, C_6H_4); 135.54, 136.61, 148.80, 150.99 (C_{ipso}). Anal. Calcd. for $C_{33}H_{26}FeO$: C, 80.17; H, 5.29; Fe, 11.29. Found: C, 80.29; H, 5.08; Fe, 11.42%.

3.5. The action of tetrafluoroboric acid etherate on the cyclopropene *1a*

Tetrafluoroboric acid etherate (3 ml) was added dropwise with stirring and cooling (−40 to −50 °C) in an atmosphere of dry nitrogen to a solution of compound **1a** (0.25 g, 1 mmol) in dry ether (50 ml) and the mixture was stirred at ~ −40 °C for 1 h. The precipitate that formed was separated by decantation, washed with several portions of cold ether (decantation) and dried in vacuo with an external cooling. The tetrafluoroborate **6** was obtained in a yield of 0.19 g (61%), dark brown finely crystalline powder, decomposes at ~170 °C. ^{1}H-NMR, δ: 1.56 (4H, br.s, 2 CH_2), 4.28 (5H, s, C_5H_5), 4.35 (2H, m, C_5H_4), 5.72 (2H, m, C_5H_4). Anal. Calcd. For $C_{13}H_{13}BF_4Fe$: C, 50.06; H, 4.20; Fe, 17.90. Found: C, 49.80; H, 4.02; Fe, 18.19%.

3.6. Reaction of the cyclopropyl cation *6* with N,N-dimethylaniline

A solution of *N*,*N*-dimethylaniline (1 ml) in dichloromethane (10 ml) was added dropwise with stirring and cooling (−50 °C) in a dry inert atmosphere to a solution of the salt **6** (0.15 g, 0.5 mmol) in dichloromethane (20 ml). The mixture was stirred at −50 °C for 30 min and quenched by addition of water (50 ml). The organic layer was separated, washed with 5% HCl (2 × 10 ml) and water, dried with Na_2SO_4, and concentrated. Chromatography of the residue (Al_2O_3, hexane-ether, 7:1) afforded 1-(*p*-dimethylaminophenyl)-1-ferrocenylcyclopropane 7, 0.11 g (60%), orange oil. ^{1}H-NMR, δ: 1.24–1.32 (4H, m, 2 CH_2), 3.01 (6H, s, 2 CH3), 3.72 (2H, m, C_5H_4), 3.98 (2H, m, C_5H_4), 4.10 (5H, s, C_5H_5), 6.51 (2H, d, C_6H_4, $J = 8.2$ Hz), 6.74 (2H, d, C_6H_4, $J = 8.2$ Hz). Anal. Calcd. for $C_{21}H_{23}FeN$: C, 73.05; H, 6.71; Fe, 16.18; N, 4.06. Found: C, 72.84; H, 6.93; Fe, 16.12; N, 3.89%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 187751 for exo-2-ferrocenyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambrige CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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